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ANTISTATIC TRANSPARENT COATING COMPOSITIONS

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ANTISTATIC TRANSPARENT COATING COMPOSITIONS

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Claim

- 1. Antistatic transparent coating compositions containing organic binders and electrically conductive powders, wherein the organic binders comprise hydroxyl group-containing copolymers and urethane elastomers as the principal components, said copolymers comprise hydroxyl group-containing vinyl monomer and vinyl chloride as the principal components, and the electrically conductive powders contain tin oxide as the principal component and have a particle diameter of $0.2~\mu m$ or less.
- 2. Antistatic transparent coating compositions according to Claim 1, wherein the hydroxyl group-containing copolymers contain 2-30 mol% hydroxyl group-containing vinyl monomer, 70-98 mol% vinyl chloride, and 0-28 mol% of other polymerizable monomers.

- 3. Antistatic transparent coating compositions according to Claim 1, wherein the weight ratio of the hydroxyl group-containing copolymers and the urethane elastomers is 1:4~4:1.
- 4. Antistatic transparent coating compositions according to Claim 1, wherein the content of electrically conductive powders is 100~350 parts by weight per 100 parts by weight of the organic binders.
- 5. Antistatic transparent coating compositions according to Claim 1, wherein the coating compositions further contain bifunctional or higher functional isocyanate compounds.

Detailed explanation of the invention

Industrial application field

The present invention relates to antistatic coating compositions, particularly coating compositions which can form coating films having antistatic function, transparency, excellent abrasion resistance, chemical resistance, and durability.

Prior art

According to their uses, the antistatic effect is needed in semiconductor wafer storage containers, cooling benches, cooling rooms, electronic and electric parts, floor materials and wall materials of semiconductor fabrication plants. Therefore, these materials have been coated with coating materials containing carbon powder or metal powder or are molded by mixing polymers with carbon fibers, metallic fibers, and the like until now. However, the coating films or molded articles by the conventional method are opaque and the contents can not be seen through since the films or the molded articles themselves are colored. Thus, sections requiring electrification prevention cannot be used in window parts. There is also the drawback of carbon powder coming off due to friction of the coating film surface.

Transparent coating compositions having antistatic function are disclosed in Japanese Kokai Patent Application No. Sho 57[1982]-85866. These coating compositions are obtained by including electrically conductive fine powders having a particle diameter of 0.2 µm or less and containing antimony-containing tin oxide as the principal component in binders for coating compositions. In these coating compositions, it is difficult to disperse highly the electrically conductive powders and it is also difficult to reveal stably the transparency and the antistatic function of coating films formed on polymer parts.

Problem to be solved by the invention

An objective of the present invention is to provide coating compositions excellent in transparency and antistatic function. Another objective of the present is to provide coating

compositions which can form coating films excellent in abrasion resistance, chemical resistance, and durability maintaining the antistatic effect and transparency for a long time.

Means to solve the problem

The present invention was completed based on new knowledge obtained by the present inventor et al. that when a hydroxyl group-containing copolymer is included in the organic binders of coating compositions electrically conductive powders in the coating compositions are effectively dispersed, further when a urethane elastomer is included in the organic binder component the abrasion resistance of the resulting coating films is notably improved. Therefore, the antistatic transparent coating compositions of the present invention contain organic binders and electrically conductive powders, wherein the organic binders comprise hydroxyl group-containing copolymers and urethane elastomers as the principal components, said copolymers comprise hydroxyl group-containing vinyl monomer and vinyl chloride as the principal components, and the electrically conductive powders contain tin oxide as the principal component and have a particle diameter of 0.2 µm or less, and by these coating compositions the aforementioned objectives are accomplished.

As the hydroxyl group-containing vinyl monomer, which is a constituent component of the hydroxyl group-containing copolymer of the present invention, there are hydroxyalkyl (meth)acrylates such as hydroxyethyl (meth)acrylate (this indicates both hydroxyethyl acrylate and hydroxyethyl methacrylate), hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, hydroxyoctyl (meth)acrylate, and the like; polyethylene glycol mono(meth)acrylate with an ether bond repeating number of about 2-9; polypropylene glycol mono(meth)acrylate with an ether bond repeating number of about 2-6. Such hydroxyl group-containing vinyl monomer is contained at 2-30 mol% and preferably 5-20 mol% in the hydroxyl group-containing copolymer. If the amount is too low, the electrically conductive powder cannot be homogeneously dispersed and the resulting coating films are inferior in transparency and smoothness. If the amount is too high, the coating films are inferior in chemical resistance.

The content of vinyl chloride in the hydroxyl group-containing copolymer is 70-98 mol% and preferably 80-95 mol%. Coating films having excellent chemical resistance are obtained by addition of vinyl chloride.

As the constituent component of the hydroxyl group-containing copolymer, polymerizable monomers having no hydroxyl groups may be contained. As such polymerizable monomers, there are styrene, vinyl acetate, (meth)acrylic ester, olefin, and the like. They are contained at an amount of 0-28 mol%.

The aforementioned monomers are synthesized to hydroxyl group-containing copolymers by a conventional polymerization method, for example, the solution polymerization method, emulsion polymerization method, suspension polymerization method or block polymerization method. These hydroxyl group-containing copolymers are also synthesized by copolymerizing vinyl acetate, instead of hydroxyl group-containing vinyl monomer, with monomers other than the hydroxyl group-containing vinyl monomer and saponifying the resulting copolymers.

As the urethane elastomer, there are polycondensates of isocyanate and linear saturated polyester, polycondensates of isocyanate and linear saturated polyether, polycondensates of isocyanate and caprolactam, and the like. As isocyanates, there are 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 1,3-xylene diisocyanate, 1,4-xylene diisocyanate, 1,5-naphthalene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethylbiphenylene diisocyanate, 4,4'-biphenylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, dicyclohexylmethane diisocyanate, and the like. Linear saturated polyesters are obtained by polycondensation of polyhydric alcohol and saturated polybasic acid. As the polyhydric alcohol, there are, for example, ethylene glycol, diethylene glycol, glycerin, 1,4-butanediol, 1,6-hexanediol, sorbitol, neopentyl glycol, and 1,4-cyclohexanedimethanol. As the saturated polybasic acid, there are, for example, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, succinic acid, adipic acid, and sebacic acid. As the linear saturated polyether, polyethylene glycol, polypropylene glycol, polytetraethylene glycol, and the like are exemplified.

Since the aforementioned urethane elastomers are contained as the organic binder component, coating films excellent in the abrasion resistance are obtained. The weight ratio of the hydroxyl group-containing copolymer and the urethane elastomers is 4:1~1:4. If the content of urethane elastomers is too low, the coating films are inferior in the abrasion resistance. If it is too high, coating films having excellent transparency can not be obtained since the electrically conductive powder is not sufficiently dispersed.

When bifunctional or higher functional isocyanate compounds are mixed in the coating compositions, the organic binder component is crosslinked after film formation to become a three-dimensional network structure. Therefore, the mechanical property such as abrasion resistance of the coating film is improved. As the bifunctional or higher functional isocyanate, for example, diisocyanates described above are exemplified. The isocyanates are contained at an amount of 1-20 wt% based on the organic binder.

The electrically conductive powder in the coating compositions comprises tin oxide as the principal component and its particle diameter is less than 0.2 μm and preferably 0.1 μm or less. To increase the electrical conductivity, for example, a small amount of ammonia may be added. To secure excellent electric conductivity and transparency of coating films, the

electrically conductive powder is contained at an amount of 100-350 parts by weight and preferably 120-300 parts by weight per 100 parts by weight of the organic binder. If the content of the electrically conductive powder is too low, the sufficient electric conductivity of coating films can not be obtained even though its dispersion state is sufficient and thus the antistatic function, which is an objective of the present invention, can not be displayed. If it exceeds 350 parts by weight, the dispersion of fine powder is deteriorated since it becomes over-dense and, as a result, the transparency of coating films is damaged.

The coating composition of the present invention is prepared by dissolving the aforementioned organic binder in an organic solvent and mixing it with a tin oxide-based electrically conductive powder. As the organic solvent, conventional organic solvents are used if they can dissolve the organic binder. As the organic solvent, there are, for example, methyl ethyl ketone, cyclohexanone, toluene, ethyl acetate, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, and the like. They may be suitably mixed and used. To sufficiently disperse fine powders in the coating compositions, machinery and tools generally used for dispersing and mixing of coating compositions, such as sand mills, ball mills, high-speed rotation stirrers, three-roll rollers, and the like can be used. To further improve the dispersing of the fine powders, dispersion aids such as silane coupling agent, titanate coupling agent, surfactant, oleic acid, lecithin, and the like may be jointly used. To enhance the durability of coating films, UV absorbents or stabilizers may be mixed, and various coating compositions may be mixed within the range of not damaging the transparency of coating films for coloration.

Operation

The antistatic transparent coating compositions prepared as above of the present invention are coated objects by a conventional coating method such as the spray process, roll coater process, flow coater process, bar coating process, doctor blade process, dipping process, etc.

The coating films obtained as above have a surface intrinsic resistivity of $10^6 \Omega/\text{sq}$ or less and satisfactory electric conductivity and thus excellent antistatic effect is obtained.

Application examples

Hereinaster the present invention will be explained by application examples.

Application Example 1

(A) Preparation of a coating composition: A hydroxyl group-containing copolymer (S-Lec EHA; Sekisui Chemical Co.) containing 10 mol% 2-hydroxypropyl acrylate and 90 mol% vinyl chloride (50 g) and Nippolan 2302 (Nippon Polyurethane Co.) as polyurethane elastomer

- (50 g) (solid basis) were added to a mixed solvent containing methyl ethyl ketone 600 g and methyl isobutyl ketone (600 g). The organic binder solution thus obtained and a tin oxide-based powder (T-1, Mitsubishi Metal Co.) having average particle diameter of 0.1 µm and less 200 g were put in a ball mill. After dispersing for 48 h, 5 g (solid basis) of Colonate L (Nippon Polyurethane Co.) as an isocyanate compound were added to prepare a desired coating composition.
- (B) Preparation of coating film and its performance evaluation: The coating composition obtained in (A) was coated at a thickness of 1 μm on a polyester film by roll coater and dried by evaporating the solvent. As the electric property of the coating film, its surface intrinsic resistivity was measured based on the testing method of ASTM D-257. As transparency, the total light transmittance and haze were measured based on the testing method of ASTM D-1003. Further, for the abrasion resistance, the haze was measured after rotating 100 times under a load of 20 g by a taper testing machine using a CS-10 abrasion ring. The haze increase after the taper abrasion testing was calculated and used as an index of abrasion. The values are shown in the table below.

Application Example 2

- (A) Preparation of a coating composition: A coating composition was prepared in the same manner as in Application Example 1 (A) except that S-Lec A (Sekisui Chemical Co.) containing vinyl alcohol about at 8 mol%, vinyl chloride at about 90 mol%, and vinyl acetate at about 2 mol% was used as the hydroxyl group-containing copolymer.
 - (B) Preparation of coating film and its performance evaluation:

The performance evaluation was carried out using the coating composition obtained in (A) by the same method as that used in Application Example 1 (B). The results are shown in the table below.

Application Example 3

- (A) Preparation of a coating composition: A coating composition was prepared in the same manner as in Application Example 1 except that 70 g of S-Lec A as the hydroxyl group-containing copolymer, 30 g (solid basis) of Nippolan 3022 (Nippon Polyurethane Co.) as urethane elastomer, and 15 g of (solid basis) Colonate L as the isocyanate compound were used.
 - (B) Preparation of coating film and its performance evaluation:

The performance evaluation was carried out in the same manner as in Application Example 1 (B) except that the coating composition prepared in (A) was spray coated at a thickness of 2 μ m on a vinyl chloride resin plate.

Comparative Example 1

- (A) Preparation of a coating composition: A coating composition was prepared in the same manner as in Application Example 1 (A) except that 100 g of S-Lec EHA were used as the organic binder and polyurethane elastomer was not added.
 - (B) Preparation of coating film and its performance evaluation:

The performance evaluation was carried out using the coating composition obtained in (A) by the same method as that used in Application Example 1 (B). The results are shown in the table below.

Comparative Example 2

- (A) Preparation of a coating composition: A coating composition was prepared in the same manner as in Application Example 3 (A) except that 100 g of S-Lec EHA were used as the organic binder and polyurethane elastomer was not added.
 - (B) Preparation of coating film and its performance evaluation:

The performance evaluation was carried out in the same manner as in Application Example 1 (B) except that the coating composition prepared in (A) was spray coated at a thickness of 2 μ m on a vinyl chloride resin plate.

	Surface intrinsic resistivity (Ω /sq)	Total light transmittance (%)	Haze (%)	Haze increase after taper test (%)
Application				
Example 1	$2x10^6$	87	7	12
Application				
Example 2	$1x10^{6}$	88	8	11
Application				
Example 3	$2x10^{6}$	79	7	10
Comparative				
Example 1	$2x10^{6}$	88	6	25
Comparative				
Example 1	1x10 ⁶	78	9	29

Effect of the invention

The antistatic transparent coating compositions of the present invention can form coating films having high transparency and an excellent antistatic effect. The coating films are extremely excellent even in the abrasion resistance and chemical resistance. Further, the application range of the coating compositions is notably wider than conventional antistatic coating compositions since coating films having excellent durability maintaining the antistatic effect and transparency for a long time are formed.